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# INVESTIGATION OF TWO-PHASE TUNGSTEN-RHENIUM ALLOYS FOR IONIZER APPLICATIONS

VOLUME II

by

M. E. Kirkpatrick and R. A. Mendelson

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**TRW** SYSTEMS

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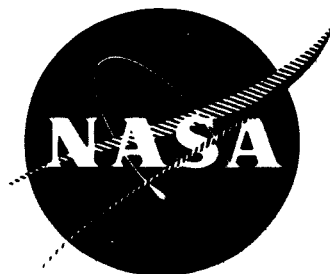
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July 1966

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Technical Management  
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ABSTRACT

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The development of porous materials from a cast two-phase alloy of tungsten-rhenium has been investigated in detail with regard to its suitability and applicability to porous ionizer materials. The laboratory program involved a study of the microstructure as a function of alloy composition over the range from 25 to 45 w/o Re. It was demonstrated that alloys in the range of 36 to 38 w/o Re had optimum proportion and configuration of the tungsten solid solution and the sigma phase alloy components. An extensive investigation into phase removal techniques for removing the sigma phase component are reported and indicate an electrolytic etching technique to be optimum in terms of reproducibility and efficiency. Cesium ionization tests were performed using a button-shaped emitter having a diameter of approximately 1/8 inch and a discussion of the ionizer test results is discussed.

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## I. INTRODUCTION

The development of porous materials for use in contact ion engine systems has been based upon powder metallurgy techniques during the past several years. These developments have led to porous materials prepared from spherical powders which result in sintered structures having surface pore densities which range up to  $8 \times 10^6$  pores per  $\text{cm}^2$  and average pore diameters which are in the range between two and three microns. Ionizers prepared from such materials have demonstrated good performance, but there still appears to be a need for porous structures of greater porosity and surface pore density.

Based upon this need, this laboratory undertook a study to investigate and evaluate techniques other than powder metallurgy for the preparation and production of porous metal structures. The results of this study indicated that a unique method based on the removal of a second phase alloy component from a two-phase metal structure may have certain advantages for ion engine applications. A survey of binary alloy systems suitable for this technique was carried out and resulted in the selection of the tungsten-rhenium system. Figure 1 shows the equilibrium phase diagram for the tungsten-rhenium system (reference 1). As will be noted from the diagram, the tungsten-rich alloys are composed of a single solid solution phase denoted as  $W_{ss}$ . The tungsten-rich intermediate phase, which is denoted sigma, occurs at approximately 50 per cent rhenium and has wide solubility limits. It is the two-phase region between the tungsten solid solution field and the sigma field which is of interest to the current program. All alloys which have compositions between 30 and 40 w/o Re are thus composed of two distinct metallic phases. Each phase is presumably enough different chemically to allow the chemical removal of one phase in the presence of the other. From the diagram, it can be seen that an alloy prepared in this composition range will, upon cooling, first form dendrites of the tungsten solid solution composition. Upon subsequent cooling through

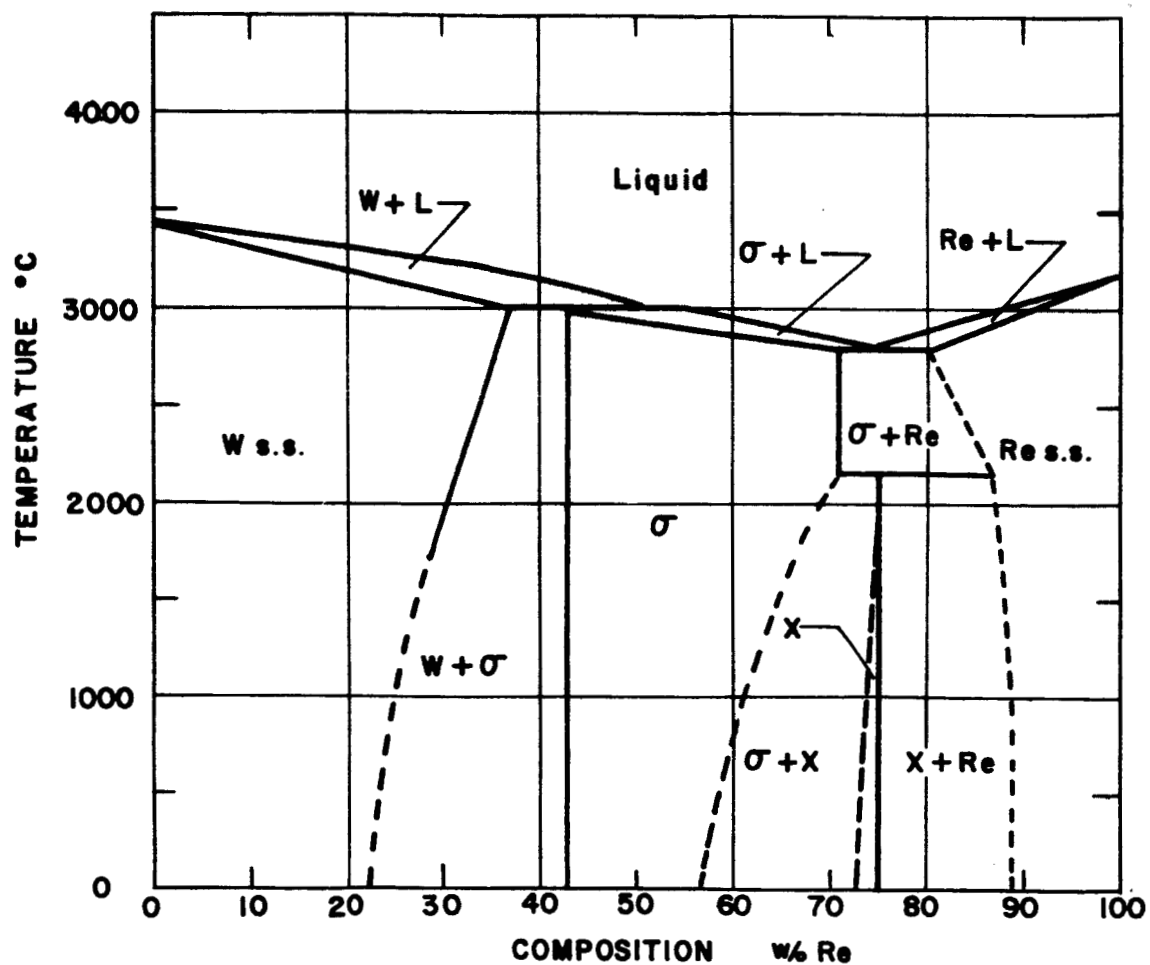


Figure 1

Equilibrium Phase Diagram for the Tungsten-Rhenium  
System After Dickinson, et al.

the solidus temperature, the remaining liquid will solidify forming sigma phase.

The objectives of the current program involve detailed investigations of two-phase tungsten-rhenium alloys in an effort to demonstrate concept feasibility.

## II. LABORATORY INVESTIGATIONS

### A. Microstructure Studies

The preliminary laboratory investigation involved the study of arc-cast microstructures of tungsten-rhenium alloys ranging in composition from 25 w/o Re to 45 w/o Re. A series of 16 alloys covering this composition range were prepared by arc-casting in an inert-gas arc furnace. Each alloy charge had a total weight of approximately 15 grams and resulted in an arc-cast button suitable for metallographic investigations. Table I lists each of the alloys prepared along with observed hardness and density data. Figures 2 through 7 are photomicrographs of selected alloy compositions and reveal the typical microstructures observed for alloys in this composition range. The objective of this preliminary alloy survey was to determine the optimum composition range for the alloy studies to be carried out during the remainder of the program. This composition range was found to lie between 37 and 38 w/o Re, with the majority of the subsequent alloys prepared at 37.5 w/o Re. Figures 8 and 9 represent typical microstructures observed at the optimum composition and reveal microstructures potentially suitable for ionizer applications.

The arc-casting process for the preparation of alloys results in a nonuniform structure. Figure 10 represents a cross section of a 37.5 w/o Re alloy and shows the variation in microstructure of the cast ingot. This variation results from the casting process which produces a heat treating effect on the unmelted portion of the alloy button near the bottom of the casting. The upper two-thirds of the cast alloy ingots have a more uniform dendritic structure which is the alloy structure of interest to the current laboratory investigations.

The present investigations further involve the relationship between alloy cooling rate and alloy microstructure. These investigations were again carried out within the inert-gas arc furnace and were performed, in general, on extremely small alloy charges. As would be expected, these

TABLE I  
Tungsten-Rhenium Alloy Survey

<u>Alloy Composition w/o Re</u>	<u>Alloy Hardness Rockwell C</u>	<u>Alloy Density gms/cm<sup>3</sup></u>
25	42	19.52
27	44	19.57
29	45	19.61
30	46	19.60
31	48	19.58
32	50	19.62
33	51	19.64
34	53	19.65
35	57	19.64
36	59	19.67
37	57	19.65
38	59	19.63
39	58	19.42*
41	--	19.37*
43	--	19.36*
45	--	19.53*

\* Porosity noted from metallographic examination.

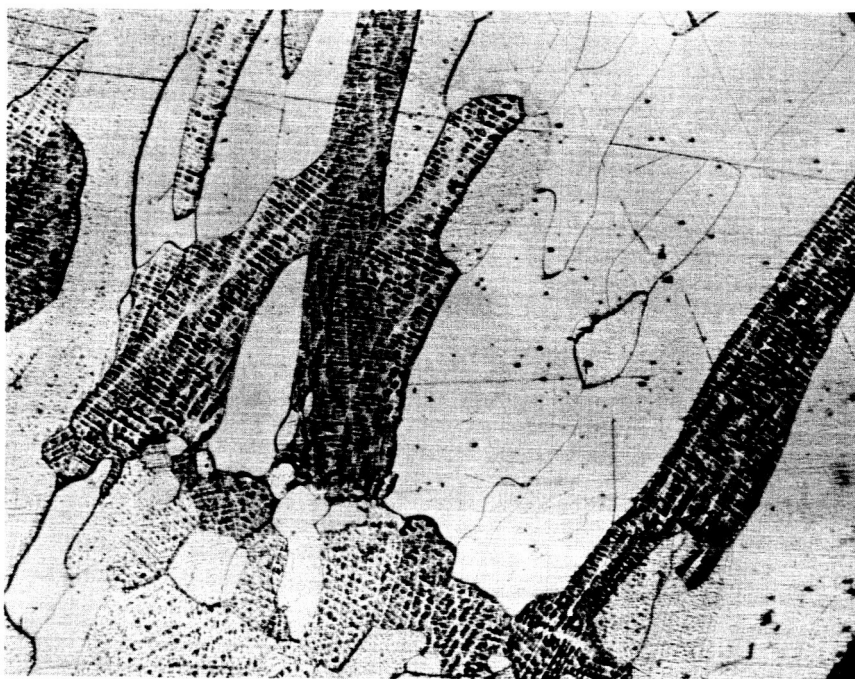


Figure 2. Photomicrograph of a 29 w/o Re-Tungsten Alloy  
As Cast. X50

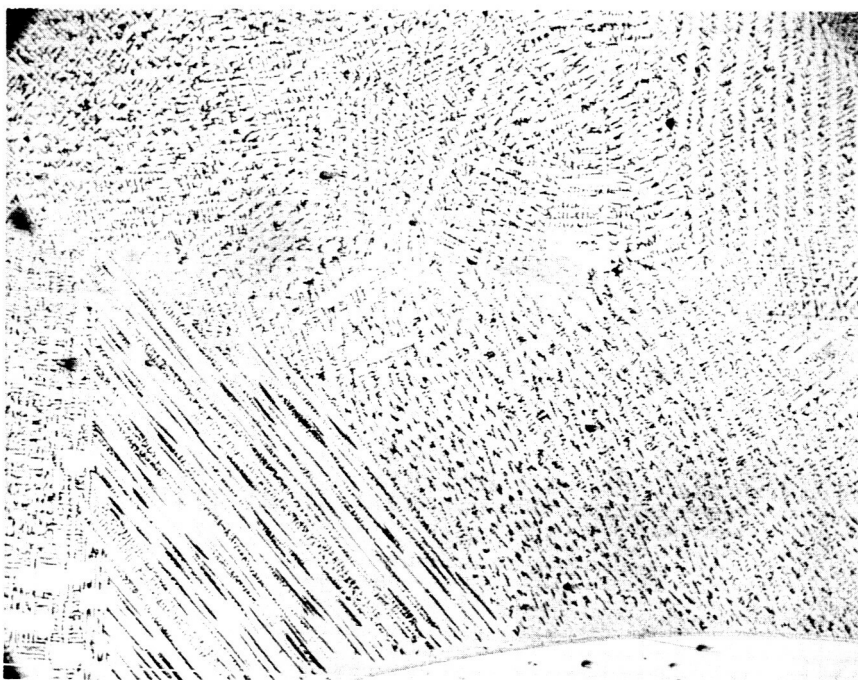


Figure 3. Photomicrograph of a 31 w/o Re-Tungsten Alloy  
As Cast. X50

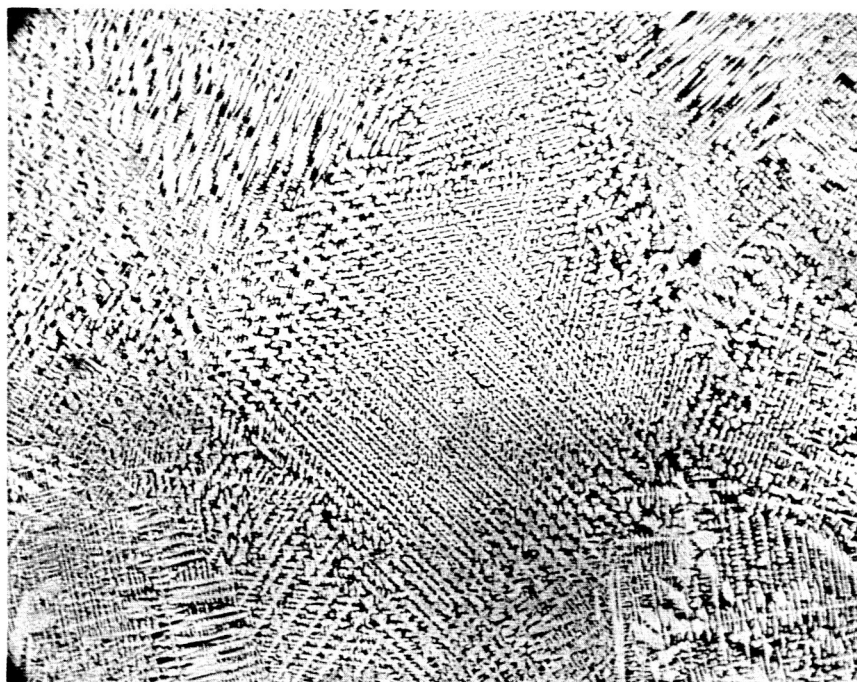


Figure 4. Photomicrograph of a 34 w/o Re-Tungsten Alloy  
As Cast. X50

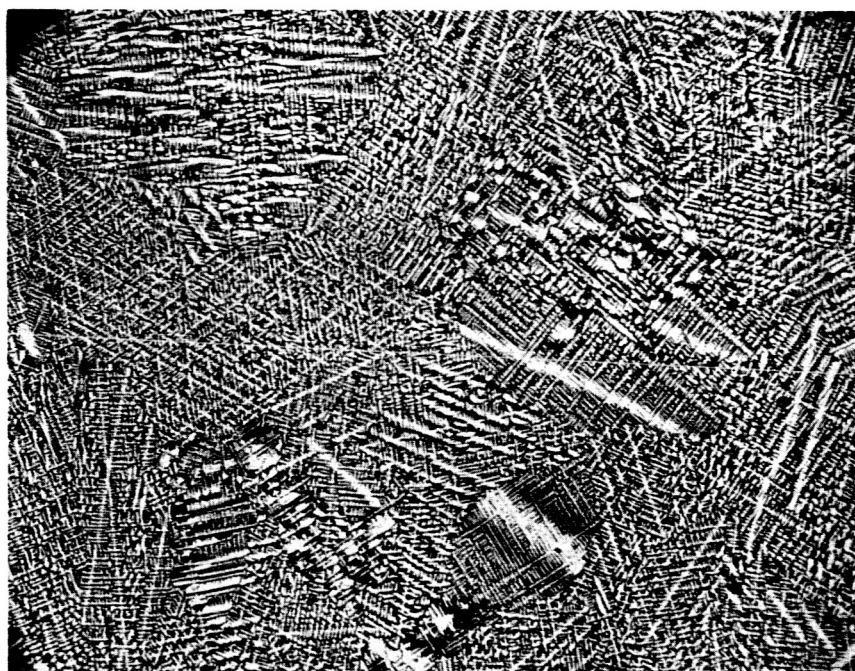


Figure 5. Photomicrograph of a 36 w/o Re-Tungsten Alloy  
As-Cast. X50

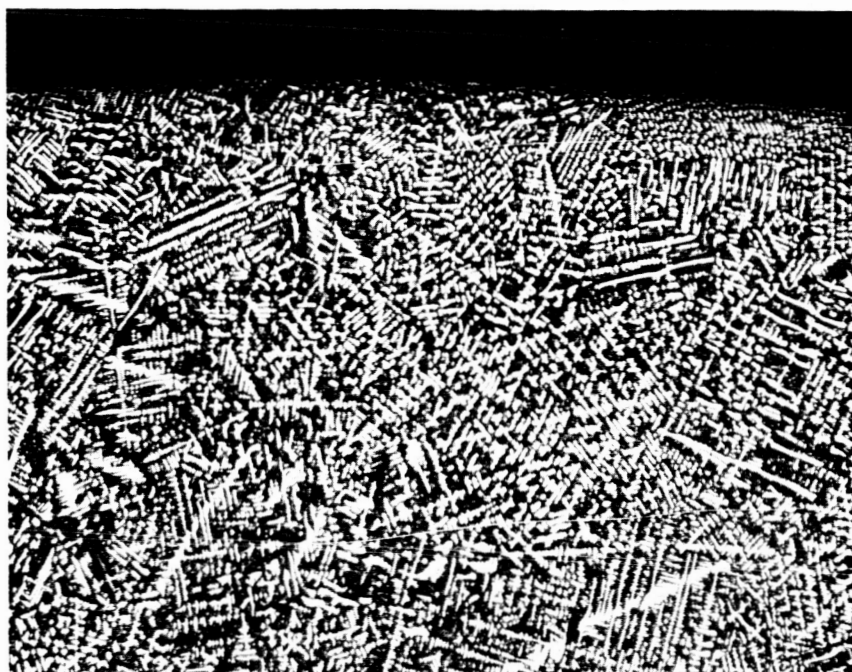


Figure 6. Photomicrograph of a 38 w/o Re-Tungsten Alloy  
As Cast. X50



Figure 7. Photomicrograph of a 41 w/o Re-Tungsten Alloy  
As Cast. X50



Figure 8. Photomicrograph of the As-Cast Tungsten Solid Solution Dendrites in a 36 w/o Re-Tungsten Alloy. X200



Figure 9. Photomicrograph of the As-Cast Tungsten Solid Solution Dendrites in a 37 w/o Re-Tungsten Alloy. X200



Figure 10

Section of an Arc-Cast 37.5 w/o Re Alloy

studies show a direct correlation between cooling rate and dendrite size within the cast structure. Figure 11 shows a typical microstructure of a rapidly cooled 37.5 w/o Re alloy and reveals an extremely fine dendritic structure which results in average pore sizes less than two microns. A preliminary effort to determine the surface pore density on such a structure has resulted in effective surface pore densities exceeding  $10 \times 10^6$  pores per  $\text{cm}^2$ .

The microstructure studies have revealed that the optimum two-phase structure is obtained from alloys in the composition region between 37 and 38 w/o Re and that such alloys, through rapid cooling procedures, can result in porosity characteristics which exceed any realized to date through powder metallurgy techniques. Therefore, it would appear that two-phase tungsten-rhenium alloys can produce microstructures which potentially exceed powder metallurgy porosity parameters believed to be of importance for ionizer applications.

#### B. Phase Removal Studies

The phase removal investigations which have been carried out during this program have entailed various chemical reactions processes for the removal of sigma phase alloy in the presence of tungsten solid solution. Preliminary investigations using separate alloys of the sigma phase and solid solution phase compositions revealed that concentrated nitric acid was effective in dissolving sigma phase alloys and, further, that the reaction rate on tungsten solid solution alloys was negligibly small. Therefore, a series of investigations were undertaken involving alloys in the composition range between 37 and 38 w/o Re in an effort to produce porous alloy structures. These studies were all carried out using concentrated nitric acid at room temperature. These efforts resulted in the observation of an insoluble reaction product at the sigma phase-acid interface. Both X-ray diffraction and spectrographic techniques were employed to determine the composition of this reaction product which was

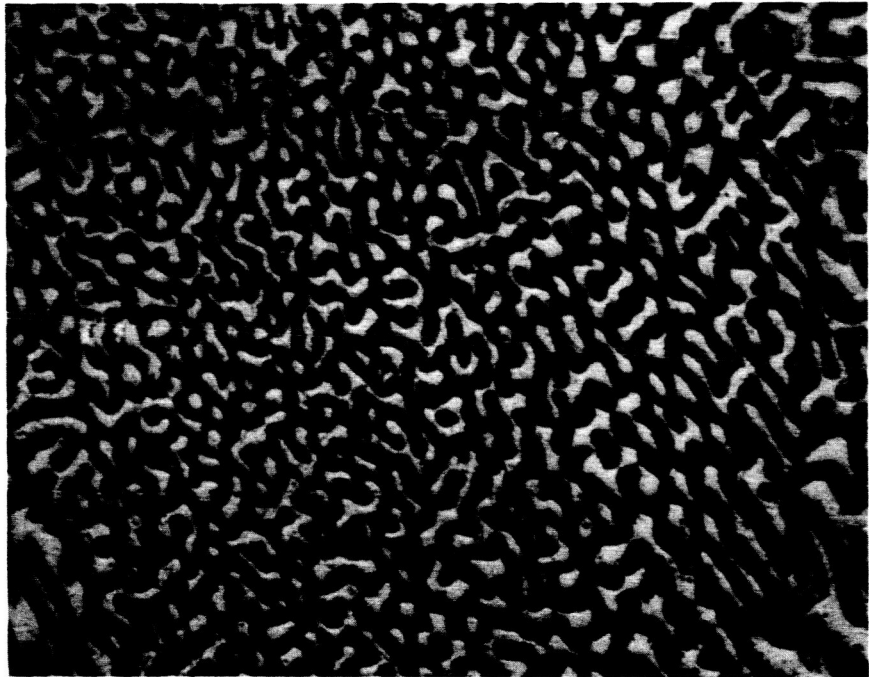


Figure 11  
Microstructure of a Rapidly Cooled W-37.5 w/o Re Alloy.  
X1000

found to be a form of tungstic acid and, therefore, soluble in a basic solution. Based upon these results, the phase removal process was modified to employ ammonium hydroxide as an intermediate step between each acid reaction process. This method was found to be only partially effective in producing porous alloy structures. A series of 0.020 inch thick alloy slabs were prepared from arc-cast buttons and used in these investigations. Metallographic sections of these alloy slabs revealed effective removal of sigma phase component to the depth of approximately 0.005 inches. Further attempts to effect phase removal to greater depths from the exterior alloy surface were not successful. It appears that, although there is a significant difference in the reaction rates between sigma phase and tungsten solid solution with nitric acid (approximately 1000:1), upon effecting phase removal to some partial depth, the ratio of available surface area of the solid solution phase becomes excessively large in comparison to the available surface area of the sigma phase alloy. This factor thus results in the continuous removal of the solid solution phase after the removal process has reached the critical depth.

Based on these observations, a new series of laboratory investigations were undertaken to study other possible phase removal processes in an attempt to enhance the reaction rate differential between the two alloy phases. A series of studies involving the reaction rates in nitric acid at elevated temperatures was carried out. It was found from these studies that some improvement in reaction rate was observed, but this improvement appeared to be only slight and did not result in a significant improvement of porous alloy structures. Further examination of the use of chemical etching procedures indicated that the primary controlling process was the formation of the inhibiting oxide layer which effectively reduced the leverage factor previously observed to approximately a 1:1 ratio. Inasmuch as the tungsten oxide layer tended toward a suboxide ( $\text{WO}_2$ ) formation as shown by the color film formation (reference 2), it was concluded that techniques leading toward a more straightforward oxidative mechanism would

prove effective. In this respect, an apparatus was constructed which allowed both variations in temperature and "acid strength" to be cursorily examined. This study showed that bubbling oxygen through the acid etcher gave more rapid phase removal rates, with greater penetration, but that ultimately the same limiting removal rates became dominant. Inasmuch as this corresponds to the viscous layer concept (reference 3) found in various chemical etching and polishing processes, it was concluded that, although the basic concept was proved, a reasonably rapid procedure based on a strictly chemical procedure would entail more extensive studies on etchant velocities and geometries which were outside this particular investigation.

Another study involving electrochemical phase removal (electroetching) processes was initiated. Examination of the oxidation-reduction couples of both tungsten and rhenium show that they are reasonably complex in acid solutions. In basic solutions, however, tungsten has only one valence transformation (+6) and rhenium transformations are limited to three ( $\text{Re}^0 \rightarrow \text{Re}^{+4}$ ,  $\text{Re}^{+4} \rightarrow \text{Re}^{+7}$ , and  $\text{Re}^0 \rightarrow \text{Re}^{+7}$ ). Since the efficiency of any electrochemical process is directly dependent on the valence change, with maximum efficiency occurring if there can be a single valence step, electroetching in a basic solution was indicated.

Examination of electropolishing and electroetching methods indicated that for maximum removal of material, the solution should be heated for increased reaction rate, agitated in order to allow maximum electrolyte interaction, and of moderate concentration in order to allow reasonable reaction selectivity. Thus, the operating parameters were established at an electrolyte concentration of 0.5 N sodium hydroxide, and 80° C bath temperature with agitation. Etching voltage was varied from two to five volts DC, and a 0.5 volt AC ripple was imposed in order to enhance the corrosion action of the electrolyte. Examination of the buttons after electroetching showed that the sigma phase was preferentially removed with minimal attack of the solid solution. This was particularly true at

the lower etching voltages. The time required to completely penetrate the buttons and produce a porous structure was enormously reduced over that of chemical etching; seven mil ionizer buttons were electroetched in twenty minutes as compared to thirty or more hours for the nitric acid etch method.

### III. IONIZER FABRICATION AND TESTING

A further objective of this program involved the preparation and fabrication of a porous emitter button which could be evaluated through cesium ionizer testing. Based on the preliminary phase removal processes discussed above, the first attempts at producing ionizer buttons were unsuccessful. The first attempt involved the use of alloy slabs having a total thickness of .020 inches and resulted in sections which were nonuniformly etched. This nonuniformity resulted from a slab which had a thickness too great for the phase removal process. Therefore, the next attempt to fabricate ionizer buttons involved alloy sections having a total thickness of 0.010 inches. A series of six ionizer buttons were prepared in this manner for potential use in an ionizer test module. During the fabrication of ionizer test modules, a rhodium braze is employed to produce the seal between the porous plug and the ionizer plenum chamber. It was observed from the several braze attempts on these ionizer buttons that the rhodium braze liquid completely infiltrated both the front and rear surface of the ionizer plug. Therefore, the remaining ionizer buttons were retained for electron beam welding attempts to produce the necessary high temperature seal. Four such ionizer modules were welded in-house, and all resulted in cracked or porous weld joints unsuitable for further ionizer testing. Figures 12 and 13 are photomicrographs of typical electron beam welded assemblies prior to phase removal processing and reveal potential crack patterns as well as some porosity in the weld zone. In addition, one ionizer module assembly was forwarded to NASA/Lewis Research Center for electron beam welding assembly. The ionizer button appeared to be cracked following this welding assembly and, therefore, no further ionizer testing could be accomplished.

During the course of further phase removal studies, it was found that electrolytic etching procedures could be employed to produce the desired porous metal structures. The use of electrolytic techniques allow masking procedures which result in preparation of porous structures uniquely



Figure 12. Electron Beam Weld Area Between Molybdenum and Fully Dense Tungsten-Rhenium Alloys. 100X



Figure 13. Electron Beam Weld Area Between Molybdenum and Fully Dense Tungsten-Rhenium Alloys. 200X

different from previous phase removal processing. This procedure has resulted in the preparation of an ionizer button having the desired porosity throughout the central section of the ionizer slab but composed of a fully dense alloy ring around the outer diameter of the ionizer button. Figure 14 shows a photograph of a typical ionizer button prepared in this manner. Through the use of this method, several buttons have been prepared for fabrication into ionizer modules through the conventional rhodium brazing technique. Three ionizer test modules were fabricated in this manner, and the ionizer data reported were obtained from one such module.

Preliminary permeability and transmissivity tests of the ionizer module revealed extremely low emitter porosity. Bubble tests indicated interconnecting porosity only over specific regions of the button surface. Based on previous difficulties in interpreting bubble test results, it was concluded to proceed with the ionizer test. The ionizer test results also revealed poorly interconnecting porosity within the ionizer material. Ion current densities of less than  $1 \text{ ma/cm}^2$  were achieved assuming the full area of the ionizer face. Attempts to determine the electron work function of alloy ionizers were compromised by the presence of the molybdenum plenum chamber structure. The investigation of neutral fraction with temperature did not produce acceptable neutral levels. It would appear from these tests that the alloy ionizer was porous over an extremely small portion of the total ionizer area.

The postmetallographic analysis of the ionizer module revealed a significant amount of remaining sigma phase alloy throughout the central portion of the alloy ionizer slab. Figure 15 shows the cross section of the test ionizer, and it is clear from these data that less than 1 per cent of the total emitter area was contributing to cesium flow.

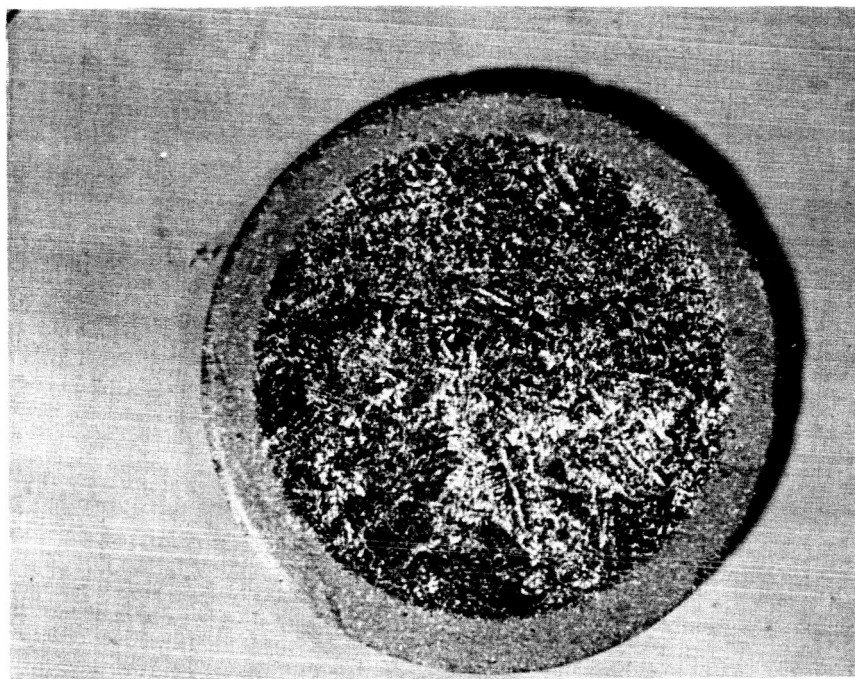


Figure 14. Photograph of an Electrolytically Etched Tungsten-Rhenium Ionizer Button. 20X

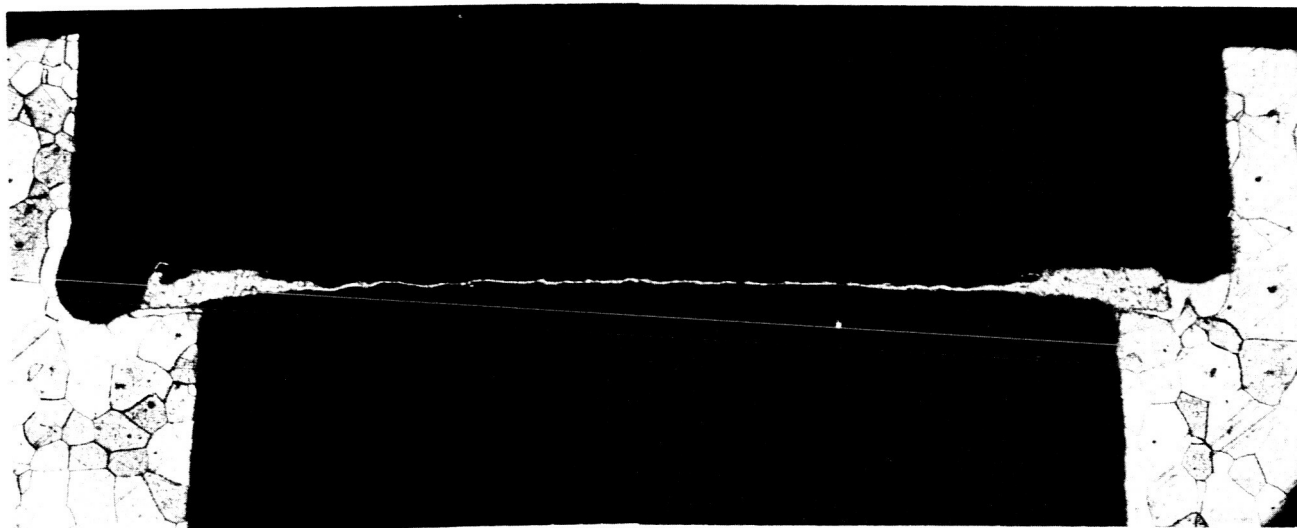


Figure 15. Cross-Section of the Ionizer Test Module Used During Ionizer Evaluation

#### IV. SUMMARY AND CONCLUSIONS

A series of laboratory investigations involving the preparation of porous materials from two-phase tungsten-rhenium alloys has been completed. These studies have shown that tungsten-rhenium alloys having a composition between 37 and 38 w/o Re have microstructures suitable for processing and fabrication of porous ionizer materials. Alloys in this composition range contain two distinct phases: tungsten solid solution and an intermetallic compound denoted as the sigma phase. Preliminary evaluation of several phase removal processes have demonstrated the feasibility of the removal of the sigma phase in the presence of the tungsten solid solution matrix phase. Ionizer buttons have been fabricated and ionizer test modules prepared for the ionizer evaluation of this type of porous material. From these studies, it would appear that the two-phase alloy ionizer concept is feasible for the preparation of porous materials suitable for ion engine applications although the current program did not produce an ionizer of uniform porosity.

## V. RECOMMENDATIONS FOR FUTURE WORK

Based upon the results of the present program, it would appear desirable to proceed with additional studies of the two-phase alloy ionizer concept. At this time, there appears to be four major task areas which should be pursued in detail through a subsequent laboratory program. Each of these four tasks are discussed in detail below.

### Task 1 - Minor Alloy Additions to Tungsten-Rhenium Alloys

Based on currently available data, it would appear that minor additions of other elements such as iridium to tungsten-rhenium alloys of the proper two-phase composition could potentially provide added reaction resistance of the matrix phase. It is believed that minor additions of iridium could increase the effective phase removal depths by a significant amount. Therefore, it is recommended that additional detailed studies involving ternary tungsten-rhenium alloys be undertaken to provide the added matrix chemical stability. These investigations would, again, involve detailed studies of the microstructure relationships over specific composition ranges of selected alloys.

### Task 2 - Phase Removal Process Studies

The current phase removal techniques, involving both chemical and electrochemical techniques, have been partially successful in the preparation of porous ionizer materials. However, it is believed that the present phase removal studies have been far from comprehensive and that much improvement can be realized through a series of laboratory investigations involving the detailed mechanism of phase removal. At the present time, it appears that the optimum phase removal process may involve electrolytic techniques; however, other reaction processes such as gas phase reactions should also be considered in any subsequent laboratory investigations.

### Task 3 - Fine Structure Alloy Development

The present program has demonstrated the ability to prepare extremely fine microstructures through rapid cooling from the melt. It is, therefore,

recommended that further investigations be undertaken to provide relatively large cast sections containing the desired fine microstructure. Such techniques as "splash" casting of molten tungsten-rhenium alloys should be studied in an effort to prepare thin sections of cast materials containing suitable microstructures.

#### Task 4 - Ionizer Evaluation

The development of any ionizer material must be based upon actual cesium ionizer evaluation. It is, therefore, recommended that additional emitter modules be prepared as part of this program for ionizer evaluation. Ion emitter diameters ranging from 0.156 inches to the order of 0.5 inches should be considered to obtain the most desirable module arrangement for the ionizer evaluations.

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